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MATHEMATICS

Example of a Class of Systems of Ordinary Differential Equations Having no Decision Method for Existence Problems

by

S. JAŚKOWSKI

Presented by K. KURATOWSKI on December 22, 1953

In analysis, we deal with the notion of natural number, and the non-decidability of the whole of analysis is an immediate consequence of the non-decidability of the arithmetic of integers. Nevertheless, the question whether a particular class of problems possesses a decision method or not may be interesting. The present paper gives the negative answer to that question concerning a class of existence problems for ordinary differential equations formulated by means of rational functions and rational numbers.

Put $\psi(a, b) = \frac{1}{2}(a+b)(a+b+1)+b+1$. A function $f(a_1, \ldots, a_n)$ will be called a ψ-superposition, if and only if $f(a_1, \ldots, a_n)$ can be written by means of all or some signs: $\psi, a_1, \ldots, a_n$. Let N be the set of all non-negative integers. For every $A \subset N$ we put $A^1 = A$ and $A^{-1} = N - A$. Let $\{\varepsilon_{i,j}\}$ be a finite double sequence with terms $\varepsilon_{i,j} = \pm 1$, $i = 1, \ldots, h$, $j = 1, \ldots, k$ and $f_1(a_1, \ldots, a_n), \ldots, f_k(a_1, \ldots, a_n)$ some ψ-superpositions. The question whether or not

(P) *for every subset A of N such $a_1, \ldots, a_n \in N$ and such an index $i = 1, \ldots, h$ exist that $f_j(a_1, \ldots, a_n) \in A^{\varepsilon_{i,j}}$ holds for all $j = 1, \ldots, k$*

will be called the Pepis problem determined by $\{\varepsilon_{i,j}\}$ and by the ψ-superpositions $f_1, \ldots, f_k$. The decision problem of the class of all Pepis problems is equivalent to the decision problem of the functional calculus. That is a consequence of the Pepis reduction of the decision problem of the functional calculus to a particular class of expressions and to a particular kind of arithmetical models*). Hence the class of Pepis problems possesses no decision method in virtue of the non-decidability of the functional calculus.

*) See [1] p. 325 theorem 35, and p. 290 definition of the $\varkappa$-Ausdruck.

The ψ-superpositions $f_1, \ldots, f_k$ and the sequence $\{\varepsilon_{i,j}\}$ determine the following system of differential equations (1)—(10) with dependent variables $\varrho, \sigma, \lambda_i, \mu_j, \nu_j, x, y, z_i, u_j, v_j$ and initial condition (11). For $i = 1, \ldots, n$ $j = 1, \ldots, k$, $D = \frac{d}{dt}$, we put

(1) $$D\varrho = 0$$

(2) $$DX = \varrho X \quad \text{where} \quad X = (t^2 - \tfrac{1}{4})x + t + \tfrac{1}{2}$$

(3) $$D\sigma = 0$$

(4) $$DDY = -\sigma^4 Y \quad \text{where} \quad Y = \frac{t^2 - \frac{1}{4}}{y}$$

(5) $$D\lambda_i = 0$$

(6) $$DDZ_i = -\sigma^4(1 + \lambda_i^2)^2 Z_i \quad \text{where} \quad Z_i = (t^2 - \tfrac{1}{4})(tz_i + \tfrac{1}{2}z_i - 1)$$

(7) $$D\mu_j = 0$$

(8) $$DU_j = 2\varrho(f_j(\lambda_1^2, \ldots, \lambda_n^2) + 1)U_j \quad \text{where} \quad U_j = (t^2 - \tfrac{1}{4})u_j + (t + \tfrac{1}{2})\mu_j - t + \tfrac{1}{2}$$

(9) $$DDV_j = -\sigma^4 \mu_j^2 V_j \quad \text{where} \quad V_j = (t + \tfrac{1}{2})^2 v_j + t + \tfrac{1}{2}$$

(10) $$Dv_j = 0$$

(11) $$\prod_{i=1}^{h} \sum_{j=1}^{k} (\varepsilon_{i,j} V_j - \nu_j^2)^2 = 0 \quad \text{for} \quad t = \theta.$$

A solution satisfying the equations in the whole interval $(-1, 1)$, will be called a *solution over the interval* $(-1,1)$. Hence, if for some t of the interval $(-1, 1)$, any part of an equation becomes the indeterminate form $\frac{0}{0}$, the equation is to be considered as not satisfied over $(-1, 1)$. Let us limit our further considerations to the real solutions over $(-1, 1)$. Then for t distinct from $-\frac{1}{2}$ and $\frac{1}{2}$, (4) implies $Y \neq 0$. For $t = -\frac{1}{2}$ and $t = \frac{1}{2}$ some expressions have the following fixed values:

t	X	Y	Z_i	DZ_i	U_j	V_j	DV_j
$-\frac{1}{2}$	1	0	0	1	1	0	1
$\frac{1}{2}$	2	0	0		μ_j		

Quite elementary methods give the general form of the solution of the system (1)—(10) over the interval $(-1, 1)$:

$$\varrho = \ln 2, \qquad X = 2^{t+\frac{1}{2}}, \qquad \sigma^2 = \pi,$$

$Y = C\cos \pi t$, where C is an arbitrary constant different from 0,

$\lambda_1^2, \ldots, \lambda_n^2$ are arbitrary non-negative integers,

$$Z_i = \frac{1}{\pi(1+\lambda_i^2)} \sin \pi(1+\lambda_i^2)(t+\tfrac{1}{2}), \quad \mu_j = 4^{f_j(\lambda_1^2,\ldots,\lambda_n^2)+1},$$

$$U_j = \mu_j^{t+\frac{1}{2}}, \quad V_j = \frac{1}{\pi\mu_j} \sin \pi \mu_j t,$$

v_j — arbitrary constants.

The system (1)—(10) possesses a real solution over $(-1, 1)$, satisfying the initial condition (11), if and only if such $\lambda_1, \ldots, \lambda_n$ and such an index $i = 1, \ldots, h$ exist that:

$$\varepsilon_{i,j} V_j \geqslant 0 \quad \text{for} \quad t = \theta \quad \text{and all} \quad j = 1, \ldots, k.$$

It may be proved that the Pepis problem (P) is equivalent to the problem whether or not

(D) *for every* θ *of the interval* $(-1, 1)$, *the system of equations* (1)—(10) *possesses a real solution over the interval* $(-1, 1)$, *satisfying the initial condition* (11).

In virtue of the non-decidability of the class of Pepis problems, there is no decision method for the class of problems (D).

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MATHÉMATIQUE

Sur certaines propriétés des domaines des méthodes continues de limitation

par

L. WŁODARSKI

Présenté par S. MAZUR le 9 Février 1954

Plusieurs résultats concernant ce domaine ont été publiés dans ma note antérieure [2]. Les théorèmes VIII, IX, X et XIIb sont des généralisations des théorèmes de Mazur et Orlicz [1], donnés pour les méthodes de Toeplitz, et les théorèmes I et II résultent du théorème de K. Zeller [3]. Les démonstrations complètes de ces théorèmes paraîtront dans Studia Mathematica, tome 14.

La méthode A donnée par la suite de fonctions $\{a_n(t)\}$ $(0 \leqslant t < T_A)$ est appelée *continue* lorsque

1° les fonctions $a_n(t)$ sont continues $(n = 0, 1, 2, \ldots)$,

2° il existe une suite $\{t_m\}$ $(t_0 = 0)$ convergente vers T_A telle que, pour tous les $\{\xi_n\}$, la convergence de la série

$$A(t; x) = \sum_{n=0}^{\infty} a_n(t)\xi_n$$

pour $t = t_m$ et $t = t_{m+1}$ entraîne la convergence uniforme de cette série dans l'intervalle $t_m \leqslant t \leqslant t_{m+1}$.

Le pseudo-domaine A^{**} de la méthode continue A, c'est-à-dire l'ensemble des suites x pour lesquelles la série $A(t;x)$ est convergente pour tout t est un espace complet du type F avec la norme

$$|x|_A^{**} = \sum_{n=0}^{\infty} \frac{1}{2^n} \cdot \frac{|\xi_n|}{1+|\xi_n|} + \sum_{m=0}^{\infty} \frac{1}{2^m} \cdot \frac{|x|_{A,m}}{1+|x|_{A,m}},$$

où

$$|x|_{A,m} = \sup_r \left| \sum_{k=0}^{r} a_k(t_m)\xi_k \right|.$$

$A(t;x)$, pour t fixe, est une fonctionelle linéaire (c'est-à-dire additive et continue) dans le pseudo-domaine A^{**} d'une méthode continue.

Le domaine A^* de la méthode continue A, c'est-à-dire l'ensemble des suites x qui appartiennent au pseudo-domaine A^{**} et pour lesquelles $\lim_{t\to T_A} A(t;x)$ existe, est un espace complet du type F avec la norme

$$|x|_A^* = |x|_A^{**} + |x|_A \quad \text{où} \quad |x|_A = \sup_{0\leqslant t<T_A} |A(t;x)|.$$

Convenons de dire que:

La suite $x=\{\xi_n\}$ *est limitable* par la méthode A vers le nombre ξ, si

$$1^0 \quad x \in A^*, \qquad 2^0 \quad \lim_{t\to T_A} A(t;x) = \xi.$$

La norme $|x|_1$ *est plus forte* que la norme $|x|_2$ dans l'ensemble X, si

$$x_p \in X, \ \lim_{p\to\infty} |x_p|_1 = 0 \text{ implique } \lim_{p\to\infty} |x_p|_2 = 0.$$

Les normes $|x|_1$ *et* $|x|_2$ *sont équivalentes* dans l'ensemble X, si la norme $|x|_1$ est plus forte que la norme $|x|_2$ dans l'ensemble X et inversemment.

La norme $|x|$ dans l'ensemble X des suites $x=\{\xi_n\}$ a *la propriété* (W) si

$$x_p = \{\xi_n^{(p)}\}_l \in X, \ \lim_{p\to\infty} |x_p| = 0 \text{ implique } \lim_{p\to\infty} \xi_n^{(p)} = 0 \ (n=0,1,2,\ldots).$$

Théorème I. a) *Chaque norme* $|x|$ *ayant la propriété* (W), *avec laquelle le pseudo-domaine* A^{**} *de la méthode continue* A *est un espace complet du type* F, *est équivalente à la norme* $|x|_A^{**}$ *donnée ci-dessus.*

b) *Chaque norme* $|x|$ *ayant la propriété* (W), *avec laquelle le domaine* A^* *de la méthode* A *est un espace complet du type* F, *est équivalente à la norme* $|x|_A^*$ *donnée ci-dessus.*

Théorème II. *Soient* A *et* B *des méthodes continues.*

a) *Si* $A^{**} \subset B^{**}$, *la norme* $|x|_A^{**}$ *est plus forte que la norme* $|x|_B^{**}$ *dans l'ensemble* A^{**}.

b) *Si* $A^* \subset B^*$, *la norme* $|x|_A^*$ *est plus forte que la norme* $|x|_B^*$ *dans l'ensemble* A^*.

La méthode A est appelée *permanente* si chaque suite convergente est limitable par la méthode A vers sa limite ordinaire.

Théorème III. *Pour toute méthode continue* A, *l'ensemble des suites dont presque tous les termes sont nuls est partout dense au sens de la métrique* $|x|_A^{**}$ *dans le pseudo-domaine* A^{**}.

Théorème IV. *Pour toute méthode continue et permanente* A, *l'ensemble des suites convergentes est partout dense au sens de la métrique* $|x|_A^*$ *dans l'ensemble des suites bornées limitables par la méthode* A.

Théorème V. *Soient* A *et* B *deux méthodes continues. Si la norme* $|x|_A^{**}$ *est plus forte que la norme* $|x|_B^{**}$ *dans l'ensemble des suites dont presque tous les termes sont nuls, alors* $A^{**} \subset B^{**}$.

Théorème VI. *Soient A et B deux méthodes continues et permanentes. Si la norme $|x|_A^*$ est plus forte que la norme $|x|_B^*$ dans l'ensemble des suites convergentes, chaque suite bornée limitable par la méthode A est limitable par la méthode B vers le même nombre que par la méthode A.*

Théorème VII. *L'ensemble des suites bornées $x=\{\xi_n\}$ limitables par la méthode A continue et permanente est un espace complet du type F avec la norme $|x|^*=\sup|\xi_n|$. Toute autre norme ayant la propriété (W), avec laquelle un tel ensemble est un espace complet du type F, est équivalente à la norme $|x|$.*

Théorème VIII. *Si une méthode continue et permanente ne limite que des suites bornées, elle ne limite que les suites convergentes.*

Théorème IX. *Soient A et B deux méthodes continues et permanentes. Si chaque suite bornée limitable par la méthode A est limitable par la méthode B, elle est limitable par la méthode B vers le même nombre que par la méthode A.*

Théorème X. *Si pour la méthode continue et permanente A les conditions $\{\xi_n\}\in A^*$, $\{\eta_n\}\in A^*$ impliquent $\{\xi_n\eta_n\}\in A^*$, il existe une suite d'indices (n_k) telle que, pour tout $x\in A^*$, on a $\lim\limits_{t\to T_A^-} A(t;x)=\lim\limits_{k\to\infty}\xi_{n_k}$.*

Les méthodes A et B sont appelées *compatibles*, si les suites limitables par les deux méthodes sont limitables vers les mêmes nombres.

La méthode B est appelée *plus générale* que la méthode A si $A^*\subset B^*$.

Une méthode permanente est appelée *parfaite* si elle est compatible avec toute méthode (continue) permanente et plus générale qu'elle.

Théorème XI. *Si pour tout $x=\{\xi_n\}$ appartenant au pseudo-domaine A^{**} d'une méthode continue A, et pour tout t de l'intervalle $<0;T_B)$, la suite $\{\sum\limits_{k=1}^{r}b_k(t)\xi_k\}_{r=1}^{\infty}$ est bornée, alors $A^{**}\subset B^{**}$.*

Théorème XII. *Supposons que, pour toute suite x appartenant au domaine A^* de la méthode continue A, la transformée $B(t;x)$ de la méthode continue B soit une fonction bornée.*

a) *Si A et B sont des méthodes permanentes, toute suite bornée limitable par la méthode A est limitable par la méthode B vers le même nombre.*

b) *Si A est une méthode parfaite et B une méthode permanente, la méthode B est plus générale que la méthode A.*

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THEORETICAL PHYSIC

Equations of Motion and Non-Harmonic Coordinate Conditions

by

L. INFELD

Presented on January 21, 1954

The object of this note is once more to return to the problem of motion of two bodies in general relativity theory. It is known that these equations of motion can be gained from the field equations. We shall deal here only with the first approximation to these equations, that is, with Newtonian motion only.

The Newtonian equations of motion were deduced by Fock [1] from the field equations and the harmonic coordinate-condition. Fock's deduction gives the impression that the harmonic coordinate condition plays an essential role in the derivation. We shall show here that the Newtonian equations of motion can be deduced from another, non-harmonic, coordinate-condition, by a method similar to Fock's. This is so, because the coordinate-condition has, in reality, nothing to do with the equations of motion not only in the Newtonian but also in the next approximation after the Newtonian. Or, in other words, the approximation procedure used by Fock and by us [2], [3] is sufficiently stringent to ensure a proper coordinate-system. No other equations in the form of harmonic or other coordinate-conditions need be added.

We shall start with the formulas used in [2], [3], [4]. There we introduced:

$$g_{\alpha\beta} = \eta_{\alpha\beta} + h_{\alpha\beta}, \tag{1}$$

where $\eta_{\alpha\beta}$ is:

$$\eta_{00} = 1;\ \eta_{0k} = 0;\ \eta_{mk} = -\delta_{mk}. \tag{2}$$

Here and later Greek indices run from 0 to 3 and Latin indices from 1 to 3. (Repetition of indices implies summation). Then we introduce $\gamma_{\alpha\beta}$ through the equation:

$$\gamma_{\alpha\beta} = h_{\alpha\beta} - \tfrac{1}{2}\,\eta_{\alpha\beta}\,\eta^{\sigma\varrho}h_{\sigma\varrho}. \tag{3}$$

We use now the gravitational equations $R_{\alpha\beta} = 0$ into which we introduce the γ's of the following order:

$$\begin{aligned} &\gamma_{00} \quad \text{of the order two:} \quad \underset{2}{\gamma_{00}} \\ (4) \qquad &\gamma_{0k} \quad \text{of the order three:} \quad \underset{3}{\gamma_{0k}} \\ &\gamma_{kl} \quad \text{of the order four:} \quad \underset{4}{\gamma_{kl}}. \end{aligned}$$

Thus we are led to the following equations:

$$\begin{aligned} &\underset{2}{\gamma_{00,ss}} = 0 \qquad \left(\gamma_{\alpha\beta,\sigma} = \frac{\partial \gamma_{\alpha\beta}}{\partial x^{\sigma}}\right) \\ (5) \qquad &\underset{3}{\gamma_{0m,ss}} = 0 \\ &\underset{4}{\gamma_{mn,ss}} = 2 \underset{4}{A_{mn}}, \end{aligned}$$

where $\underset{4}{A_{mn}}$ is a function of $\underset{2}{\gamma_{00}}$ and $\underset{3}{\gamma_{0m}}$ which we shall not specify at the moment. Equations (5) are the gravitational equations for empty space, modified by the following coordinate-conditions:

$$\begin{aligned} &\underset{3}{\gamma_{0r,r}} - \underset{2}{\gamma_{00,0}}\,\underset{1}{} = 0, \\ (6) \qquad &\underset{4}{\gamma_{mr,r}} = 0. \end{aligned}$$

Here the placing of "1" under the zero in $\underset{2}{\gamma_{00,0}}$ requires some explanation, which will also clarify the reason that equations (5) follow from the gravitational equations. We assume, and this is essential for the approximation method used, that the motion is quasistationary; that is, that the differentiation with respect to time lowers the order of the quantity used. Thus $\underset{2}{\gamma_{00,0}}$ is of the third order.

Now let us return to equations (5) and write down their solutions. We assume that the solutions represent singularities of the field. Of course we are well aware that singularities do not properly represent masses with continuous density distribution. But we are concerned here with masses of which we can assume central symmetry, with masses, the motion of which is represented by the motion of their centre. We are concerned with their fields outside matter. Therefore we may represent these masses by singularities of the field. For the sake of simplicity we shall assume only two masses with the coordinates

$$(7) \qquad \eta^s(t) \quad \text{and} \quad \zeta^s(t).$$

Then as a solution of (5) we take for $\underset{2}{\gamma_{00}}$:

$$(8) \qquad \underset{2}{\gamma_{00}} = -4 \overset{1}{\underset{2}{m}}(r)^{-1} - 4 \overset{2}{\underset{2}{m}}(r)^{-1} = 2\varphi.$$

Here $\overset{1}{m}_2$ is the mass of the first particle and it is of the order two. Similarly $\overset{2}{m}_2$ is the mass of the second particle. Then $\overset{1}{r}$ is:

$$(9\,a) \qquad \overset{1}{(r)}^2 = (x^s - \eta^s)(x^s - \eta^s).$$

Similarly:

$$(9\,b) \qquad \overset{2}{(r)}^2 = (x^s - \zeta^s)(x^s - \zeta^s).$$

Now $\underset{3}{\gamma}_{0m}$ must be, according to (5), a harmonic function satisfying equation (6):

$$(10) \qquad \underset{3}{\gamma}_{0r,r} = \underset{2}{\gamma}_{00,0}\,\underset{1}{} = 4\,\overset{1}{\underset{2}{m}}\overset{1}{(r)}_{,r}^{-1}\dot{\eta}^r + 4\,\overset{2}{\underset{2}{m}}\overset{2}{(r)}_{,r}^{-1}\dot{\zeta}^r,$$

from which follows:

$$(11) \qquad \underset{3}{\gamma}_{0r} = 4\,\overset{1}{\underset{2}{m}}\overset{1}{(r)}^{-1}\dot{\eta}^r + 4\,\overset{2}{\underset{2}{m}}\overset{2}{(r)}^{-1}\dot{\zeta}^r.$$

We turn now to the last equation in (5) which we shall write out explicitly:

$$(12) \qquad \underset{4}{\gamma}_{mn,ss} = -\underset{3}{\gamma}_{0m,0n}\,\underset{1}{} - \underset{3}{\gamma}_{0n,0m}\,\underset{1}{} + 2\,\delta_{mn}\varphi_{,00} - 2\,\varphi\varphi_{,mn} - \varphi_{,m}\varphi_{,n} + \tfrac{3}{2}\,\delta_{mn}\varphi_{,s}\varphi_{,s}.$$

We are looking for the solution of this equation in the neighbourhood of the first particle. Also we are looking only for those expressions which are of the order zero in $(x^s - \eta^s)$. The first three expressions on the right hand side of (12), that is the linear terms, give the following solution in the neighbourhood of the first particle:

$$(13) \qquad -2\,\overset{1}{m}\overset{1}{(r)}^{-1}\{(x^n - \eta^n)\ddot{\eta}^m + (x^m - \eta^m)\ddot{\eta}_n - \delta_{mn}(x^s - \eta^s)\ddot{\eta}^s\}.$$

It is slightly more difficult to find the solution for the nonlinear terms. As we are looking only for those parts of γ_{mn} which are of the order zero in $x^s - \eta^s$, we are interested only in those expressions on the right hand side of (12), which are of the order "—2". These are:

$$(14) \qquad -4\,\overset{1}{\underset{2}{m}}\overset{2}{\underset{2}{m}}\{\partial_{\eta^s}(r)^{-1}(x^s - \eta^s)\overset{1}{(r)}_{,mn}^{-1} + \partial_{\eta^m}(r)^{-1}\overset{1}{(r)}_{,n}^{-1} + \partial_{\eta^n}(r)^{-1}\overset{1}{(r)}_{,m}^{-1} - 3\,\partial_{\eta^s}\overset{1}{(r)}^{-1}\overset{1}{(r)}_{,s}\delta_{mn}$$

where

$$r^2 = (\eta^s - \zeta^s)(\eta^s - \zeta^s).$$

As can easily be verified, the solution of this part of the right hand side of (12) is

$$(15) \qquad 2\,\overset{1}{\underset{2}{m}}\overset{2}{\underset{2}{m}}\partial_{\eta^s}(r)^{-1}\left\{\frac{(x^m - \eta^m)(x^n - \eta^n)(x^s - \eta^s)}{\overset{1}{r^3}} + 2\,\delta_{mn}\frac{x^s - \eta^s}{\overset{1}{r}}\right\}.$$

Thus $\underset{1}{\gamma}_{mn}$ is the sum of (13) and (15) in all the expressions in $(x^s - \eta^s)$ of order zero.

Now we wish $\underset{4}{\gamma}_{mn,n}$ to equal zero. As this must be true for every power of $(x^m - \eta^m)$ it must be true for powers "-1". We see by direct calculation of

$$\underset{4}{\gamma}_{ms,s} \sim \{\text{equ}\,(13) + \text{equ}\,(15)\}_{,s}, \tag{16}$$

that we have for expressions of the order "-1" in the neighbourhood of the first particle:

$$\underset{4}{\gamma}_{mr,r} = -4\,\underset{2}{m}(r)^{-1}\{\ddot{\eta}^m - \underset{2}{m}\,\partial_{\eta^m}(r)^{-1}\}. \tag{17}$$

Thus the coordinate condition is only satisfied if

$$\ddot{\eta}^m = \underset{2}{m}\,\partial_{\eta^m}(r)^{-1}, \tag{18}$$

that is, if the Newtonian equation of motion is valid. However, we know that the equations of motion [2] can be found by some surface integrals of $\underset{4}{\Lambda}_{mn}$ which do not depend on $\underset{4}{\gamma}_{mn}$ at all. Therefore, contrary to appearances, the equations of motion have nothing to do with the coordinate condition $\underset{4}{\gamma}_{mn,n} = 0$. A less obvious point is that even in the next approximation the equations of motion have nothing to do, not only with the coordinate condition $\underset{4}{\gamma}_{mn,n} = 0$, but also with the coordinate condition $\underset{2}{\gamma}_{00,0} - \underset{1}{\gamma}_{0s,s} = 0$ [3, 5].

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THEORETICAL PHYSICS

Electrodynamics with Higher Derivatives as a Particular Case of Electrodynamics with Non-Linear Equations

by

Z. SZYMAŃSKI

Presented by L. INFELD on January 21, 1954

Infeld and Plebański in their paper, "Electrodynamics without Potentials" indicated the possibility of a general treatment of the problems of electrodynamics [1]. A framework was given from which equations (for the most part non-linear) for the electromagnetic field were derived. A characteristic feature arising out of this framework consists in employing the field tensor without using the potentials. The electromagnetic potential appears here as a secondary quantity. The Maxwell equations follow from this theory as a limiting case as a result of using the variational principle with the restrictive condition.

Podolsky and Schwed [2] presented a linear theory of the electromagnetic field by using the higher derivatives in the variational formalism. The field equations deduced in this way are partial differential equations of the third order with respect to the field tensor. Since the equations derived in [1] are of an order less than three, it is obvious that a theory with higher derivatives cannot be deduced from the general framework introduced in [1].

It appears, however, that there is a possibility of formulating a theory (non-linear in general) with higher derivatives, similar to the theory demonstrated in paper [1]. It is also possible to avoid introducing the electromagnetic potential as a starting quantity. From such a theory we shall get a linear theory with higher derivatives [2] similar to the Maxwell theory following from the electrodynamics without potentials, i. e. by using the variational principle with the restrictive condition.

We shall begin by introducing the skewsymmetrical electromagnetic field tensor:

$$P_{\alpha\beta} = -P_{\beta\alpha}$$

(the physical meaning: — the tensor $p_{\alpha\beta}$ is defined by the vectors of the electric displacement $\vec{D}$ and the magnetic field $\vec{H}$). Infeld and Plebański [1],

obtain the current four-vector by forming a divergence of the field tensor:

$$p_{\alpha\beta,\beta} = j_\alpha .$$

Now we shall change the current definition slightly and shall assume

$$j_\alpha = (1 - a^2\Box) p_{\alpha\beta,\beta},$$

where a is a constant with the dimension of length.

We shall now introduce the assumption that the Lagrange function H depends only on two invariants:

$$H = H(P, \varrho),$$

where:

$$P = -\tfrac{1}{4} p_{\alpha\beta} p_{\alpha\beta}$$
$$\varrho = (j_\alpha j_\alpha)^{1/2} = \{(1 - a^2\Box) p_{\alpha\beta,\beta} \cdot (1 - a^2\Box) p_{\alpha\gamma,\gamma}\}^{1/2}.$$

The Euler equations of the variational principle,

$$\delta \int H d_{(4)} x = 0,$$

can be written in the form:

$$\frac{\partial H}{\partial p_{\alpha\beta}} - \left(\frac{\partial H}{\partial p_{\alpha\beta,\gamma}}\right)_{,\gamma} + \left(\frac{\partial H}{\partial p_{\alpha\beta,\gamma\delta}}\right)_{,\gamma\delta} - \left(\frac{\partial H}{\partial p_{\alpha\beta,\gamma\delta\varepsilon}}\right)_{,\gamma\delta\varepsilon} = 0.$$

Introducing notations

$$H_{(P)} = \frac{\partial H}{\partial P}, \qquad H_{(\varrho)} = \frac{\partial H}{\partial \varrho},$$

we get after particular calculations the following field equations:

$$H_{(P)} p_{\alpha\beta} = \left\{(1 - a^2\Box)\left(\frac{H_{(\varrho)} j_\beta}{\varrho}\right)\right\}_{,\alpha} - \left\{(1 - a^2\Box)\left(\frac{H_{(\varrho)} j_\alpha}{\varrho}\right)\right\}_{,\beta}.$$

Now we may put

$$H_{(P)} p_{\alpha\beta} = f_{\alpha\beta}$$
$$(1 - a^2\Box)\left(\frac{H_{(\varrho)} j_\alpha}{\varrho}\right) = A_\alpha .$$

We see that the new skewsymmetrical field tensor (defined by vectors $\vec{E}$ and $\vec{B}$) is the four-dimensional curl of a certain four-vector:

$$f_{\alpha\beta} = A_{\beta,\alpha} - A_{\alpha,\beta}.$$

In the currentless case, i. e. when

$$j_\alpha \equiv (1 - a^2\Box) p_{\alpha\beta,\beta} = 0,$$

we may obtain from the aforesaid theory the equations of Podolsky's linear theory by using the variational principle with the Lagrangian

$$L = H(P) + B_\alpha j_\alpha ,$$

where B_α is an undetermined function (four-vector — Lagrange's multiplier).

The variational principle

$$\delta \int L d_{(4)} x = 0,$$

from which follow the Euler equations with higher derivatives to the third order inclusive, permits us to write

$$H_{(P)} p_{\alpha\beta} = (1 - a^2 \Box)(B_{\beta,\alpha} - B_{\alpha,\beta}),$$

and in an another form we have

$$f_{\alpha\beta} = A_{\beta,\alpha} - A_{\alpha,\beta},$$

where A_α is defined as follows:

$$A_\alpha = (1 - a^2 \Box) B_\alpha.$$

By assuming $H = P$ we get exactly the equations of Podolsky's theory.

I wish to express my thanks to Prof. L. Infeld and to Docent J. Plebański for valuable discussions throughout the work.

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EXPERIMENTAL PHYSICS

Two Observations of Unstable Nuclear Fragments

by

P. CIOK, M. DANYSZ and J. GIERULA

Communicated by A. SOŁTAN at the meeting of February 4, 1954

In 1952 Danysz and Pniewski [1] reported a case of a peculiar coincidence of two events in nuclear emulsion. They ascribed it tentatively to a delayed decay of a heavy fragment ejected from a cosmic ray star. Soon afterwards similar observations were made in other laboratories [2], [3], [4] and [5]. Recently we have found two more cases of this type. In all these cases a multiply charged particle (further referred to as a heavy fragment or particle f) is ejected from a high energy interaction (star A). This particle, after having apparently stopped in the emulsion*), decays giving birth to a small low energy star (star B).

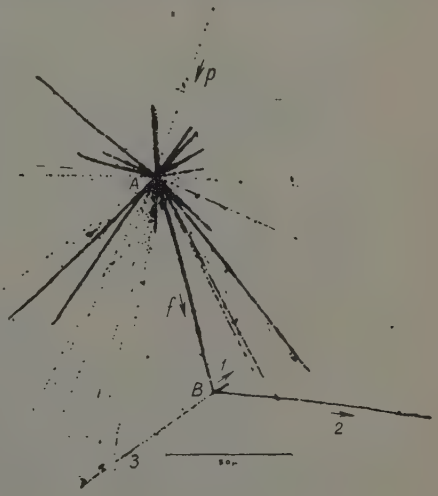

Fig. 1

The two cases found recently have occurred in a G 5 emulsion 600 μ thick, exposed in a balloon flight for eight hours at an altitude of about 25000 meters. The data concerning these two cases (event 6 and 7), together with similar data concerning the other cases of this type reported by different authors, are summarized in Table I. Table II gives the directions of tracks in the stars B for events 1, 6 and 7, while in Table III the energies of the secondaries of stars B are compared.

Event 6 (Fig. 2). The energy of the primary particle of the star A as estimated using statistical data of Camerini et al. [6] and of Daniel et

*) Perhaps with the exception of events 4 and 7.

TABLE I

Event			1	2	3	4	5	6	7
Type of star A			$21+18p$	$16+0p$	$30+30p$	$13+1p$	$24+10p$	$18+14\pi$	$18+1p$
Track f	length (μ)		90	219	68	2	30	80	13
	charge (e)		4–6	2–3	2–3	—	4–7	3–4	—
Star B	number of tracks		4	3	3	4	3	3	2
	range (μ) and grain density of track	1	10 black	24 black	1.4 recoil	2245 black	5.8 black	14 black	113 black
		2	126 black	117 black	60 black	>192 black	182 black	78 black	>330 95 gr./50 μ $R=4$ mm.*)
		3	>674 55 gr./50 μ $R=23$ mm.*)	5.1 g_{pl}	>325 2.3 g_{pl}	169 black	>759 2.56 g_{pl}	>370 80 gr./50 μ $R=6.5$ mm.*)	—
		4	2.5 recoil	—	—	>262 black	—	—	—
Authors			Danysz & Pniewski	Tidman et al.	Crussard & Morellet	Lovera et al.	Freier et al.	present work	present work

TABLE II

Event	1 (Fig. 1)				6 (Fig. 2)			7 (Fig. 3)	
Track	1	2	3	4	1	2	3	1	2
φ	0°	22°	162°	135° to 200°	0°	178°	285°	0°	137°
θ	−49°	+34°	−36°	0° to 90°	−47°	+12°	+48°	−29°	+49°

φ — angle in plane of the emulsion
θ — angle of dip

TABLE III

Event	1	2	3	4	5	6	7
Energy of secondaries (if protons) in MeV	82	48	25**)	23.6	125	40	30
	4.1	4.0	2.7	>6.5	10.4***)	3.1	3.8
	0.8	1.6	recoil	>5.4	5.2	1.0	—
	recoil	—	—	5.0	—	—	—

al. [7] is about 30 BeV. The multiply charged particle f, as deduced from the characteristics of the end of its track, appears to stop in the emulsion.

*) if proton
**) if π
***) if B^{12}

From comparison of the shape of the track f with those of other multiply-charged particles stopping in the emulsion, the charge of particle f is evaluated to be $3e$ to $4e$. The charges of the secondaries of the star B as evaluated by inspection are:

$$Z_1 - 1e \text{ or } 2e$$

$$Z_2 - 1e \text{ or } 2e$$

$$Z_3 - 1e$$

Track 3 has been followed in the facing plate for another 800 μ. Both scattering and grain-density measurements rule out the possibility of par-

Fig. 2

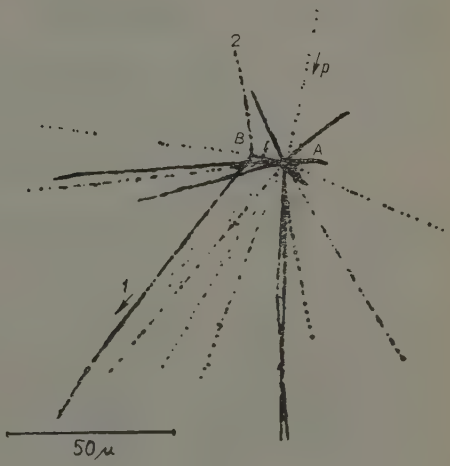

Fig 3.

ticle 3 to be a meson — being consistent with the assumption that it is a proton.

Assuming particle 3 to be a proton, we evaluated the total energy release in star B to be greater than 100 MeV.

Event 7 (Fig. 3). The energy of the primary particle of the star A is estimated to be about 5 BeV. The general appearance of the f particle track corresponds rather to an end part of a track; no definite conclusion can be drawn, however, as to its charge. The charges of the secondaries, as

evaluated by inspection, are:

$$Z_1 - 1e \quad \text{or} \quad 2e$$
$$Z_2 - 1e$$

Track 2 has been followed in the facing plate for another 800 μ so the possibility of particle 2 being a meson was ruled out. Both scattering and grain-density measurements are consistent with the assumption that it is a proton.

Assuming particle 2 to be a proton, we evaluated the total energy release in star *B* to be greater than 100 MeV.

In both cases the time of flight of the fragment must be greater than 10^{-12} sec. The comparison of the experimental data concerning the seven observed cases of production and decay of the unstable nuclear fragments (Table I and III) shows that:

1. In all the seven cases the unstable fragments are produced in interactions, the energy of which is in the range from a few to some tens of BeV.

2. These interactions correspond to more or less central collisions of a neutral or singly charged particle with a heavy nucleus of the emulsion (high N_H).

3. The life-time of the unstable fragment is longer than 10^{-12} sec.

4. The evaluation of the total energy released in their decay is consistent with a unique *Q*-value of 175 MeV but not with the value of 140 MeV.

5. In the majority of cases no mesons are observed to be emitted among the secondaries of stars *B*.

All these features support the hypothesis of the existence of a V_1^0-particle bound in the nucleus.

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CHEMISTRY

Current Potentials and Densities on Zinc Anodes in 7 N KOH in Dependence upon Time

by

J. KAMECKI and Z. ZEMBURA

Communicated by B. KAMIEŃSKI at the meeting of November 16, 1953

It was early observed [1] that zinc anodes in alkaline solutions acquire passivity at fairly high densities of current. Later it was established that at a further stage of passivity in NaOH solutions, a zinc anode becomes covered with a dark oxidic coating [2], [3]. The appearance and properties of these coatings in NaOH solutions have been examined in detail by Huber [4], [5]. In 1938 Vernon and Stroud [6] ascertained that in a 25 per cent KOH solution zinc anodes take on a polish. The results of their work however, were not confirmed by the findings of Lajner [7].

The present work describes our investigations into the behaviour of zinc anodes in 7 N KOH, which in certain aspects differs in behaviour from NaOH. In the course of research into the circumstances which give rise to the polishing of metals, a method was introduced, whereby the dependence of the tension and the anodic potential on the anodic density, and of the anodic density and the anodic potential on the tension [7] could be examined. By means of this method we had previously examined the behaviour of copper anodes in several electrolytes [8], [9]. Our measurements revealed changes in tension and density every 1 or 3 minutes. In order to find what relation the "quick" method which we applied had to the method which necessitates waiting after each measurement until a stationary state had been reestablished, we also made measurements of the dependence of the potential and anodic density on time, with various determined tensions. We measured, too, the dependence of the anodic density on the tension and of the anodic potential on the tension in 7 N KOH saturated, in varying degrees, with zinc.

Samples of zinc (PN-H-82200-NO) cut with a handsaw and with a content of 99.993 per cent zinc and dimensions of about $30 \times 20 \times 10$ mm., were used for these tests. The plates were covered with paraffin in such a way that a surface approximately 30×20 mm. (about 6 cm.^{2}) remained free. This

surface was polished with 2/0, 3/0 and 4/0 papers before being covered with paraffin and degreased in benzene. A copper plate, measuring 65×60×1 mm., was used as a cathode and was quickly covered with zinc in the course of the measurements. The apparatus used for the measurements has been described by us in a previous paper [9], the only difference being that in this case we applied one cathode, and the rheostat R_1 had a maximal resistance of 1500 ohms. The measurements of the anodic potential were taken in the manner described in our paper [8], the values being calculated first

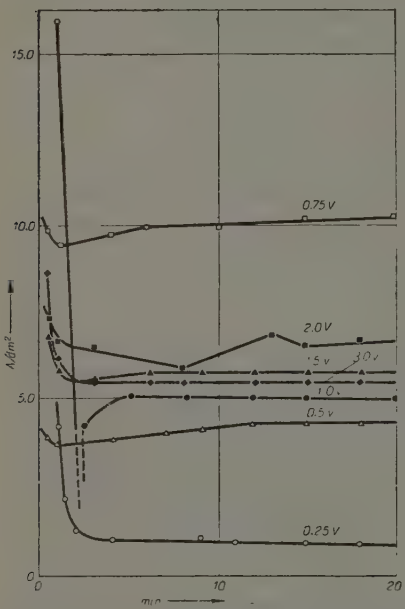

Fig. 1. Curves of dependence of the anodic density on the time (in minutes), using constant tensions (the magnitude of the tension is given beside the curves) in 7 N KOH

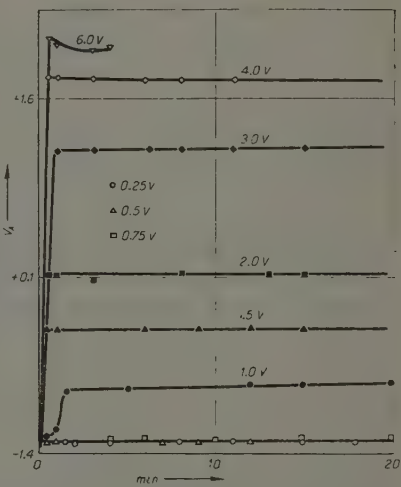

Fig. 2. Curves of dependence of the anodic potential on the time (in minutes), using constant electrolytic tensions (the magnitudes of the tension are given beside the curves) in 7 N KOH

with reference to a saturated calomel electrode and afterwards with reference to a normal hydrogen electrode.

Attention should be drawn to the fact that the bridge connecting the electrolytic cell with the intermediary cell (with KCl) was filled with KOH solution. A direct immersion of the chloride-filled bridge into the electrolysed solution causes chlorine ion diffusion, which distinctly modifies the course of the phenomena on the anode.

In order to determine the speed of the anodic processes, measurements were taken of the dependence of the anodic current density on the time,

using constant tensions of 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 3.0 and 4.0 V. The results of the measurements are given in Fig. 1.

At the same time, measurements were taken of the dependence of the anodic potential on the time (with reference to a normal hydrogen electrode), using a constant tension from 0.25 to 6 V. The result is given in Fig. 2.

Further "quick" measurements of the dependence of the electrolytic tension and anodic potential on the anodic density were taken, the anodic

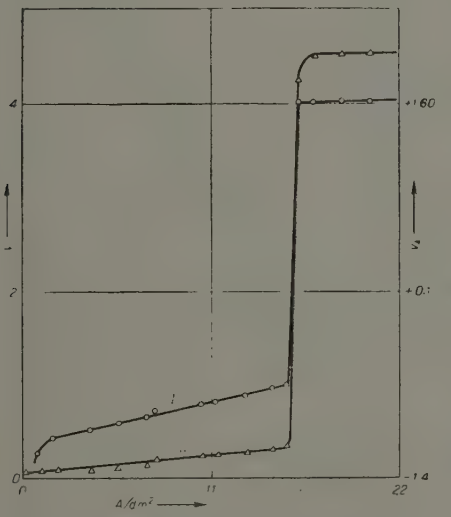

Fig. 3. Curves of dependence of the tension (I) and the anodic potential (II) on the anodic current density in 7 N KOH

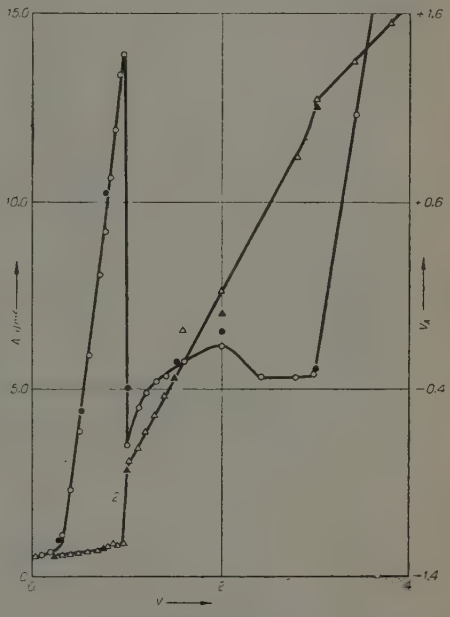

Fig. 4. Curves of dependence of the anodic current density (1) and the anodic potential (2) on the electrolytic tension in 7 N KOH

density being changed every 3 minutes. Similarly, measurements of the dependence of the anodic density of current and the anodic potential on the electrolytic tension were taken. The results are given in Figs. 3 and 4.

In Fig. 4 the measurements taken of the dependence of the anodic density on the time, using constant tensions, are also shown. The relative points of the measurements are marked by black circles or triangles.

During electrolysis the zinc becomes dissolved on the anode and partly separated on the cathode. As a result, however, of the chemical reaction between KOH and zinc, there is an increased concentration of the latter in the solution if electrolysis lasts for some time. For example, after taking the two series of measurements represented in Figs. 3 and 4, and after making several polishing tests, we found that the zinc content in the so-

lution amounted to 0.099 gram-equivalent of zinc per litre of solution. After two hours electrolysis at a tension of 2 V the concentration of zinc amounts to 0.204, and after two further hours to 0.383 gram-equivalent per litre. In proportion to the dissolution of zinc, the content of KOH in the solution decreases and the concentration of potassium zincate increases, and, therefore, in order to determine to what extent the change in the con-

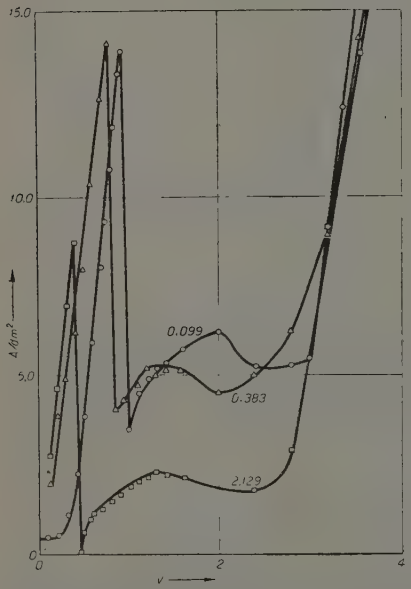

Fig. 5. Curves of dependence of the anodic density on the tension in 7 N KOH containing 0.099, 0.383 and 2.129 gram-equivalents of zinc per litre

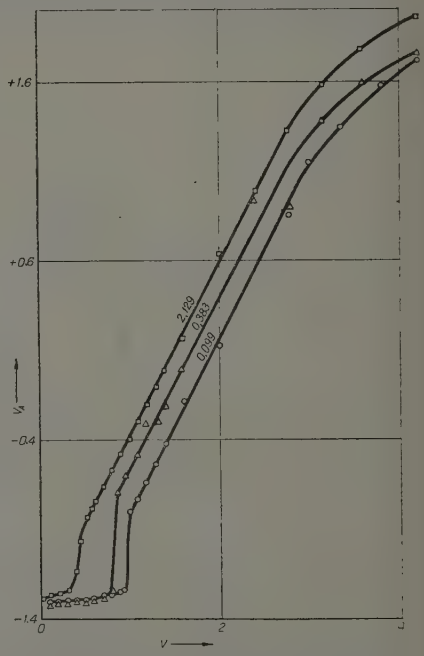

Fig. 6. Curves of dependence of the anodic potential on the tension in 7 N KOH containing 0.099, 0.383 and 2.129 gram-quivalents of zinc per litre

centration of KOH in the solution influences the course of the anodic density-tension and tension-anodic density curves, suitable measurements were taken in solutions containing 0.099, 0.383 and 2.129 gram-equivalents per litre (this last solution being obtained by dissolving zinc-dust in excess in 7 N KOH for over one year at room temperature). The results of these measurements are shown in Figs. 5 and 6.

It should be added that the zinc content in a solution containing 2.129 gram-equivalents per litre decreases after further electrolyses and polishing tests. In a pure solution of 7 N KOH polishing tests gave positive results when a tension of 4—6 V was applied for 2—3 minutes, but tracings

of crystals kept appearing on the shining surface of the zinc. On the other hand, in a solution containing about two gram-equivalents of zinc per litre, the polishing tests failed, since a coating kept forming, the latter changing in colour from black to iridescent, depending on the length of time of the electrolysis.

It was ascertained from the measurements described that the anodic current density for the determined tension was quickly established, since, as a rule, after three minutes further changes were very slight. The anodic potential (Fig. 2) is established even more rapidly, after one to two minutes. We were obliged to break off the measurements at a tension of 6 V, because the solution was rapidly becoming warm. There is close agreement between the "equilibrium" measurements and the "rapid" ones (where there is change of tension every three minutes). This is confirmed by Fig. 4, in which the "equilibrium" measurements lie along the curve of the "rapid" ones. The density-tension curves of dependence show similarity to the corresponding curves which appear during the electrolysis of phosphoric acid with a copper anode [7], with this difference only that the plateau of the curve is not flat in the case of zinc in 7 N KOH. The influence of the increasing zinc content in the KOH solution becomes evident especially in the shifting of the corresponding critical values; the shape of the curves remains in principle unchanged. The shape of the curves seems, on the basis of this, to be dependent on the KOH concentration, since in the 7 N saturated solution of zinc, the OH^- ion concentration must have fallen. The shape of the curve indicates that it fell to a value corresponding to 3 N KOH, or that $Zn(OH)_4^{--}$ ions must exist in the solution.

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CHEMISTRY

The Anodic Polishing of Zinc in KOH Solutions

by

J. KAMECKI and Z. ZEMBURA

Communicated by B. KAMIEŃSKI at the meeting of November 16, 1953

In a previous piece of research carried on by us [1], it was established, after making a series of tests on the anodic behaviour of zinc in 7 N KOH, that the measurements of tension or density taken quickly (changing every 3 minutes) are in agreement with those taken slowly. Using the apparatus

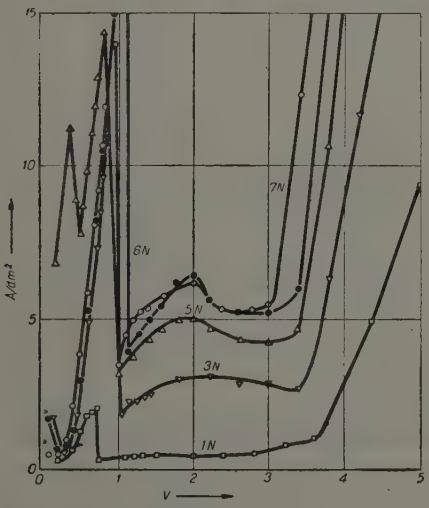

Fig. 1. Curves showing the ratio of anodic density to tension of electrolysis in 7, 6, 5, 3 and 1 N KOH

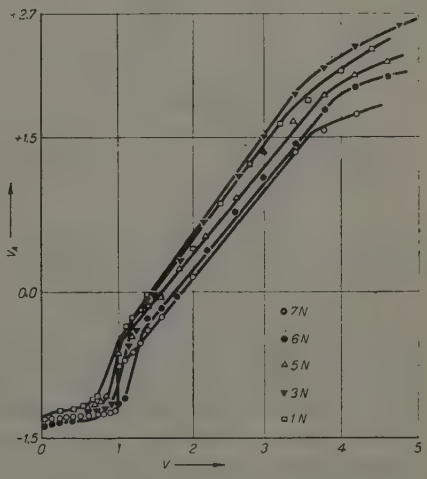

Fig. 2. Curves showing the ratio of anodic potential to tension of electrolysis in 7, 6, 5, 3, and 1 N KOH

and methods described in our previous paper, we made further tests in solutions of 6, 5, 4, 3, 2 and 1 N KOH, measuring the ratio of anodic density and anodic potential to tension, and vice-versa. On account of the great number of the measurements, only a few were selected (see Figs. 1—5).

Fig. 1 gives the measurements of the ratio of anodic density to tension of the electrolysis (the tension applied to the cathode and anode) in solutions of 7, 6, 5, 3, and 1 N KOH. At the same time the changes in anodic potential (measured with reference to a saturated calomel electrode and re-calculated with reference to a normal hydrogen electrode) are shown in Fig. 2.

The course of the processes on the anode was similar in principle in all cases. First, a whitish coating, which did not impede the flow of the current, appeared on the anode. As soon as passivity of the anode (a sudden fall in the anodic density and a sudden rise in the anodic potential) appeared,

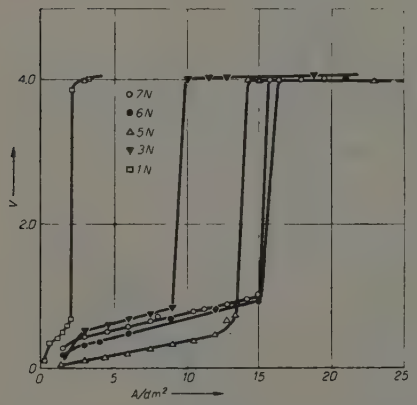

Fig. 3. Curves showing the ratio of tension potential to anodic density in solutions of 7, 6, 5, 3 and 1 N KOH

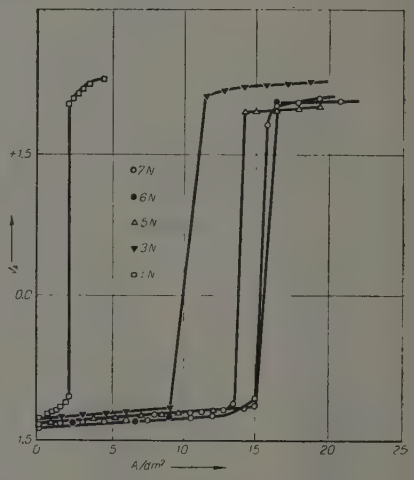

Fig. 4. Curves showing the ratio of anodic potential to anodic density in solutions of 7, 6, 5, 3 and 1 N KOH

the anode took on a metallic appearance. With further increases of tension the anode became covered with a coating, at first yellow, then brown and finally black. At a tension of about 2 V, small bubbles of gas could be seen on the anodes. Finally, when the tension was still further increased, there began a violent liberation of oxygen and the coating flaked off, leaving a shining metallic surface.

From the curves representing ratio of tension to density (Fig. 3) and of anodic potential to tension (Fig. 4), it can be seen even more clearly that as soon as the critical anodic density is exceeded, a sudden passivity of the anode appears: this is evident from the sudden rises in both the tension and the anodic potential.

On the basis of graphs showing the ratio of anodic density to tension (partially given in Fig. 1), and of tension to density (Fig. 3), the values of

the critical density, i. e. the anodic density corresponding to the sudden passivity of the anode, were determined in relation to the concentrations of KOH in the solution and drawn for purposes of comparison in Fig. 5, in which the specific electrical conductivity relating to the KOH solutions is also drawn.

The average value (the arithmetical mean of all the measurements within this range) of the density and its ratio to the concentration of KOH calculated for the plateau of the density-tension ratio curves are given in

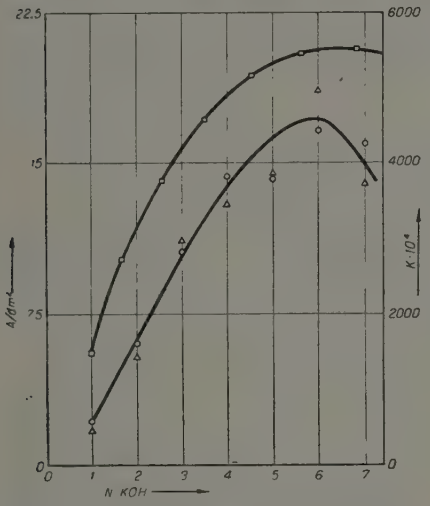

Fig. 5. Curves showing the ratio of the critical current density and specific conductivity to the concentrations of KOH in the solution (the rectangles refer to the specific conductivities, the triangles to the critical densities in the tension-density curves, and the circles to the critical densities in the density-tension curves)

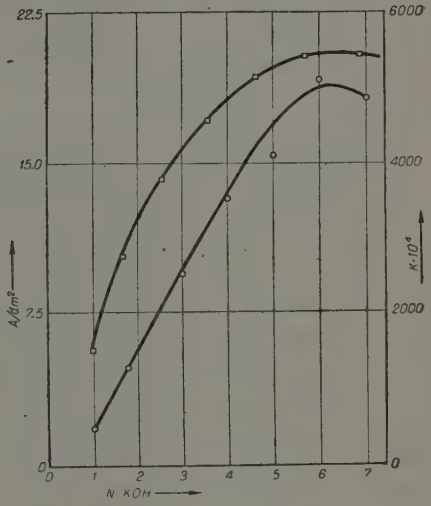

Fig. 6. Curves showing ratio of the average anodic density in the region of the plateau of the density-tension curves to the KOH concentration

Fig. 6 (circles), together with the values of the conductivities of the relative solutions (squares).

Discussion and Results. If we take all the results obtained from both the previous [1] and present researches, then we may state that:

1. The anodic tension-density ratio curves have, in all the solutions tested, the same characteristic form, and this form, moreover, corresponds to the characteristic shape of the potential-anodic density curves. From these curves the critical density may easily be read. As soon as this magnitude has been reached, passivity of the anode follows "by jump" (increase in the tension and in the anodic potential).

2. The anodic density-tension curves are still more characteristic since in these cases the section corresponding to the sudden rise in tension of the previous curves can be more thoroughly examined. These curves, also, assume a similar shape in all the solutions tested. It is interesting to note that the curves showing the ratio of density to tension often assume a similar shape in solutions in which polishing of the metals may follow [2], the only difference being that in the case of zinc the plateau is not flat.

3. Both the critical and the mean current densities in the region of the plateau are directly dependent on the current conductivity.

4. The polishing of zinc could easily be done in solutions from 7 to 3 N KOH, provided these did not contain a large amount of zincate. The optimal results for polishing were obtained in a 4 N KOH solution with a tension of about 6 V. The polishing time amounted to about 5 minutes, the temperature to c. 30°. Polishing occurs not in the region of the plateau (as in the case of copper [3]) but above it (over 3 V).

5. A coating formed on the anodes in 7—3 N KOH solutions in the region of the plateau. This coating could easily be removed by applying a tension of the order of 4 V for one to three minutes. On the other hand, despite increased tension, in solutions of 1 N KOH, in saturated solutions of zinc, and partially in 2 N KOH solutions, the coating remained.

6. The phenomena just described can be explained in the following manner: until the reaching of the maximum on the density-tension curves or until the first strong break in the tension-density curves, the anode remains active and is transferred to the solution. The value of the anodic potential at the time of electrolysis regulated by the tension amounts to about — 1.2 V; this seems to indicate that at this period zinc passes into solution as ZnO_2^{--}, while the normal potential — 1.216 corresponds to the reaction $Zn + 4\,OH^- = ZnO_2^{--} + 2\,H_2O + 2\,e$ [4]. As soon as the critical tension has been exceeded (depending on the concentration, from 1 to 0.7 V), there is a sudden fall in the anodic density and an increase in the anodic potential to a value of about — 0.8 V, which corresponds to the reaction $Zn = Zn^{++} + 2\,e$ (normal potential — 0.76 V). If the tension is further increased, the farmation of an oxide coating on the anode is initiated. Now, according to Huber [5], there follows the reaction:

$$Zn + 2\,OH = ZnO + H_2O + 2\,e.$$

At this period the thickness of the layer (though really, to be strictly accurate, on the basis of our measurements, we should speak only of the conductivity of this coating), is approximately proportional to the tension, so that the anodic density does not undergo any major changes. As soon as there is sufficient passivity of the anode, oxygen begins to be discharged on it, according to the reaction $4\,OH^- = 2\,H_2O + O_2 + 4\,e$, which corresponds to the normal potential + 0.401 V. We then observed a small diminution in the density on the density-tension curves, probably occasioned

by the closing of the pores in the coating by means of bubbles of oxygen. The anodic potential, however, increases during the whole of this period (the region of the plateau), until the sudden discharge of gases on the anode. The potential of the anode then amounts, depending on the solution, to between 1.1 and 2 V. It is possible that the reaction $OH^- = OH + e$ will then begin to take place, the normal potential in this case being $+1.4$ V. The free radical might explain the quick dissolution of the coating during this phase in solutions from 7 to 3 N KOH.

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BULLETIN DE L'ACADÉMIE
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CHEMISTRY

The Critical State of Negative Azeotropes. II. System Acetone-Chloroform

by

W. ŚWIĘTOSŁAWSKI and A. KRĘGLEWSKI

Presented by W. ŚWIĘTOSŁAWSKI on December 30, 1953

1. Introductory remarks

The results of Zawidzki's investigations [1] show that acetone and chloroform form a negative azeotrope belonging to the first group of Świętosławski's classification [2]. The critical states of different mixtures of these two components were examined by Kuenen and Robson in 1902 [3]. Small deviations from Pawlewski's rule were found in the case of these mixtures. No indication was given as to whether the compositions of the mixtures were expressed in weight or molar percentages. These authors stated only that the deviations from linear change of the critical temperature with the change in composition were positive.

The purpose of this investigation was to repeat the Kuenen-Robson experiment in order to examine more precisely the critical temperature — composition curve for the above mentioned binary mixture.

2. Experimental part

A chemically pure acetone sample was submitted to further purification by crystallization of the complex formed with sodium iodide. The crystals thus obtained were decomposed by heating and afterwards the sample was submitted to careful rectification. The boiling point was equal to $56.00 \pm 0.03^{\circ}$ C. (750 mm. Hg).

Chloroform, after being thoroughly mixed with concentrated sulphuric acid, was washed with water, dried by magnesium sulphate and then submitted to rectification. The sample boiled at $61.10 - 61.15 \pm 0.050^{\circ}$ C. (755 mm. Hg).

Both liquids were collected in containers over magnesium sulphate, dried at 800° C. For degazification of the samples air was pumped out from the containers. For filling the capillary tubes, 15 cm. long, a corresponding con-

tainer was connected to them by a tube provided with a stopcock. The liquid was introduced into the capillary tube by distillation at room temperature. Care was taken to prevent the penetration of any grease. Other details, concerning the handling of the tubes in the course of filling, pumping out the air and sealing them will be described elsewhere [4].

The capillary tubes were located in a thermostat made of duraluminium and electrically heated. The temperature T_m at which the meniscus disappeared was measured. No examination was made of the precritical region. The maximum of opalescence was more clearly pronounced in tubes containing chloroform and mixtures of acetone and chloroform with excess of the latter. The resistance for prolonged heating was examined and the heating was carried out for three hours. Pure acetone did not show any change, whereas chloroform and chloroform-acetone mixtures became yellowish. For this reason the tubes containing the mixtures under investigation were located after the thermostat had been heated to the desired temperature. In that way the appereance or disappereance of the meniscus was observed 15 – 20 minutes after the tubes had been placed in the thermostat.

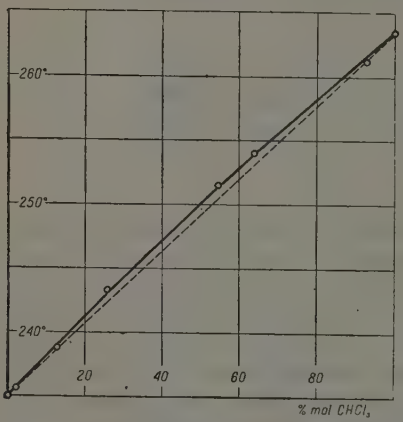

Fig. 1. Small negative deviations from Pawlewski's rule form chloroform — acetone mixture

Table I contains the results of the measurements. In the second column, symbols k, w and r correspond to the degree of filling of the capillary tubes, at which disappereance of the meniscus was observed: k — in the middle, w — in the upper part, and r — in the lower part of the tube.

TABLE I

Tube No.	Degree of filling	Composition of the mixtures				T_m °C. ± 0.05°
		weight $CHCl_3$	per cent $(CH_3)_2CO$	mole $CHCl_3$	per cent $(CH_3)_2CO$	
30	k	100.0	—	100.0	—	**263.15**
31	k	—	100.0	—	100.0	**234.95**
23	w	3.7	96.3	1.8	98.2	235.45
25	k	23.1	76.9	12.7	87.3	238.70
26	r	41.4	58.6	25.6	74.4	243.10
27	k	71.1	28.9	54.4	45.6	251.25
28	w	78.3	21.7	63.7	36.2	253.90
29	r	96.4	3.6	92.9	7.1	260.90

When plotting the observed temperature T_m against the composition of mixtures, expressed in molar percentages, small negative deviations from Pawlewski's rule (Fig. 1) were found.

Summary

1. The curve expressing the change in the critical temperatures T_m with the change in the composition of acetone-chloroform mixtures was established.

2. Small deviations from Pawlewski's rule were found. With respect to the Pawlewski straight line these deviations lie in the opposite direction to those found by Kuenen and Robson.

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CHEMISTRY

Critical State of Two-Component Systems Formed by Pyridine with Isopropyl, Isobutyl and Isoamyl Alcohols III

by

A. KRĘGLEWSKI

Presented by W. ŚWIĘTOSŁAWSKI on January 5, 1954

Isobutyl and isoamyl alcohols do not form azeotropes with pyridine [1]. Mixtures of pyridine and isopropyl alcohol have not as yet been ebuliometrically examined. It is probable, however, that these mixtures behave in the same way as those composed of pyridine and n-propanol [1].

The purpose of this investigation was to examine mixtures consisting of pyridine and the alcohols mentioned above in their critical state. In Table I are given the critical temperatures of isopropyl, isobutyl and isoamyl alcohols as determined by different investigators.

TABLE I

Substance	T_k °C	Investigator
isopropyl alcohol	234.6	Nadejdine (1882),
	238.0	de Heen (1888),
	243.47	Brown (1906),
$p_k = 53.0$ atm. isobutyl alcohol	235.0	I. C. T.
	265.0	Nadejdine (1882),
	277.63	Brown (1906),
$p_k = 48.0$ atm. isoamyl alcohol	265.0	I. C. T.
	306.6	Pawlewski (1882),
	306.9	Schmidt (1891),
	309 77	Brown (1906),
p_k unknown	307.0	I. C. T.

The critical constants of pyridine have been given in a previous paper in this series [2].

Experimental part

The alcohols were submitted twice to a careful rectification. A small amount of moisture was removed from each of the liquids by metallic sodium. The same sample of pyridine which was used in the previous experiments was submitted once more to fractional distillation The degree of purity of all of the substances was determined by using a standarized differential ebuliometer [3].

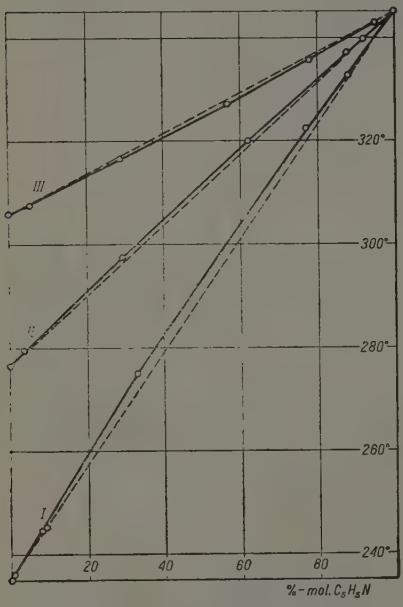

Fig. 1. Temperature T_m of the disappearance of the meniscus plotted against the molar percentage of pyridine. The dotted lines correspond to the behaviour of the mixtures obeying the Pawlewski rule. Curve *I* corresponds to the system pyridine-isopropyl alcohol; curve *II* to pyridine-isebutyl alcohol; curve *III* to pyridine-amylic alcohol

The filling of the capillary tubes and the method of measuring the temperature T_m, corresponding to the disappearance of the meniscus, were carried out in the same manner as in the previous investigations [2].

It should be noted that in all the experiments the temperature of the disappearance of the meniscus was identical with that at which the opalescence intensity reached a maximum. The opalescence was always more intensive in the case of pure pyridine and in pyridine-alcoholic mixtures than in the case of pure alcohols. Temperature T_m remained constant so long as the heating time did not exceed three hours. In these experiments the samples remained colourless.

The data obtained are presented in Tables II and III and in Fig. 1. In addition, the symbols k, w and r in Table III show whether the mean density of the systems was equal to the critical density of the corresponding mixture (k) or whether it was slightly higher (w) or slightly lower (r). This could be ascertained by noting the level in the capillary tube at which the meniscus disappeared.

The results obtained prove that the systems investigated deviate slightly from the Pawlewski rule. Two of them (I, II) show small negative deviations and the third one (III) a small positive deviation.

Taking into consideration the relatively strong influence of impurities on the measured value T_m, we can accept the critical temperature values

for isobutyl alcohol found by Brown and Nadejdine, the value T_k determined by Brown [4] should be considered as the more correct one.

TABLE II

Substance	Boiling temp. ± 0.03°	Ebull. degree of purity	T_m °C. ± 0.05°
pyridine	115.00°/749 mm. Hg	III	344.85 344.60
isopropyl alcohol	82.30°/750 mm. Hg	IV	235.25
isobutyl alcohol	107.85°/755 mm. Hg	III	276.70
isoamyl alcohol	131.85°/755 mm. Hg	III	306.05

TABLE III

No. of tube	degree of filling	weight C_5H_5N	percentage iso-C_3H_7OH	molar C_5H_5N	percentage iso-C_3H_7OH	T_m °C. ± 0.05°
32	*w*	90.6	9.4	88.0	12.0	332.50
33	*k*	81.8	18.2	77.3	22.7	322.70
34	*k*	39.2	60.8	32.9	67.1	275.05
36	*k*	11.5	88.5	9.0	91.0	245.05
35	*w*	10.5	89.5	8.2	91.8	244.50
37	*k*	1.1	98.9	0.8	99.2	236.25
		C_5H_5N	iso-C_4H_9OH	C_5H_5N	iso-C_4H_9OH	
41	*k*	92.5	7.5	92.1	7.9	339.60
41	*w*	88.4	11.6	87.7	12.3	336.40
43	*k*	63.6	36.4	62.1	37.9	320.15
44	*r*	30.3	69.7	28.9	71.1	297.40
45	*w*	3.6	96.4	3.4	96.6	279.65
		C_5H_5N	iso-$C_5H_{11}OH$	C_5H_5N	iso-$C_5H_{11}OH$	
49	*w*	94.4	5.6	94.9	5.1	342.70
50	*r*	76.1	23.9	78.0	22.0	335.30
51	*w*	53 8	46.2	56.5	43.5	326.60
52	*k*	26.2	73.8	28.3	71.7	316.55
53	*k*	4.3	95.7	4.7	95.3	307.35

Summary

1. The temperatures T_m of the disappearance of the meniscus were determined for mixtures of pyridine with isopropyl, isobutyl and isoamyl alcohols.

2. Only small deviations from Pawlewski's rule were observed for all three systems. The mixtures of pyridine with isopropyl and isobutyl alcohols show small negative deviations, and that with isoamyl alcohol a small positive one.

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CHEMISTRY

A New Colorimetric Method of the Determination of Salicylhydroxamic Acid and its Analogues

by

J. VENULET

Communicated by T. Urbański at the meeting of December 14, 1953

Since 1949, when T. Urbański [1] suggested using salicylhydroxamic acid "*T*-2" as an antitubercular agent, a number of publications relating to this problem have appeared. As a result of bacteriological, pharmacological and clinical investigations, it was found that a derivative of the above 5-bromosalicylhydroxamic acid "*T*-40" appeared to be efficient in some forms of T. B. [2]—[7].

Following upon the use of *T*-40 in clinics, there arose a new problem, namely that of finding an analytical method suitable for determining 5-bromosalicylhydroxamic acid in body fluids and in different organs. The known colour reaction of hydroxamic acids with $FeCl_3$ was found to be not sufficiently specific, as it also gives intense colour with salicylic acid and its derivatives, possessing a free phenolic group. Hydrolysis of hydroxamic acids to hydroxylamine and determining the latter with 8-hydroxycuinoline (this gives an olive-green colour) proved to be insufficiently sensitive.

In the course of our investigation we found, however, that solutions of salicylhydroxamic acid gave an intense violet colour with salts of vanadic acid in presence of mineral acids. The intensity of colour could readily be determined in a colorimeter.

Description of the method

We prepared the vanadic acid reagent by dissolving 0.25 g. of sodium or ammonium vanadate in 20 ml. 1-N sulphuric acid (without heating). The solution was completed to 100 ml. and thus was analogous to the reagent suggested by Wollenberg [8] for determining hydrazides. (It gives with hydrazides a brick-red colour). Standard solutions of known concentrations of 5-bromosalicylhydroxamic acid were used to establish the calibration

absorption curve in a Pulfrich photometer. A 610 mμ. (S 61) filter proved to be the most suitable and produced the maximum absorption.

We used 2 ml. of the examined solution, which was mixed with 1 ml. of the vanadium reagent and 2 ml. water. The greatest intensity of colour was reached after 2—3 mins. and it remained unchanged for several hours. For a certain range of concentrations the calibration curve is linear and in accordance with the Lambert-Beer law.

The minimum quantity of salicylhydroxamic acid or its bromine derivative determinable by this method is of the order of 5—10 mcg. per ml. The absorption curves for *T*-2 and *T*-40 are shown below (Fig. 1).

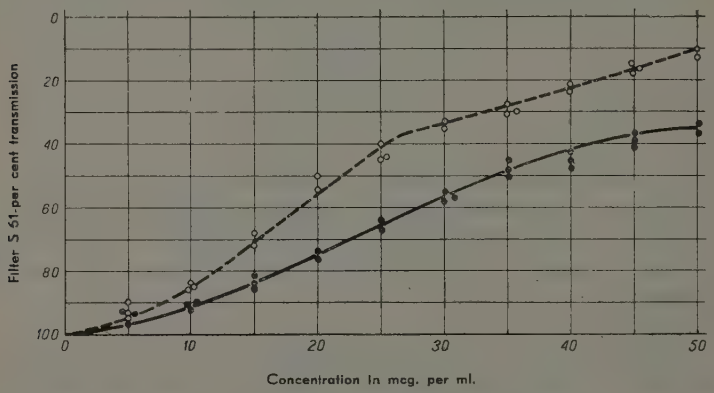

Fig. 1. *T*-2 - - - - -; *T*-40 ——

The intensity of colour depends on the acidity of the solution. It reaches a maximum only in an acid or neutral medium. When alkalised it disappears and reappears only after acidification.

The products tested by this method and the results obtained are tabulated above (Table I).

Thus it is evident that only those hydroxamic acids in which the hydroxyl group is in *ortho*-position to the hydroxamic one can give the colour-reaction. Benzhydroxamic acid (No. 3) gives a very weak colour similar to that produced by *p*-hydroxybenzhydroxamic acid (*T*-145). The product *T*-162, which does not contain a hydroxyl-group, does not give the colour reaction. Besides, the hydroxamic group here is not attached to an aromatic nucleus and therefore the acid does not posses aromatic properties. The aliphatic hydroxamic acids (e. g. No. 5) even when containing α-hydroxyl-group (such as maliohydroxamic acid, No. 6) do not give the colour reaction.

It is worth mentioning that a methoxyl-group in ortho-position to the hydroxyl-group (*T*-143) gives only a weak brick-red colour. T. Urbański [9] has suggested that this may be due to a bond formed between oxygen of

the methoxyl-group and hydrogen of the phenolic group, which would build a five-member ring.

It should be pointed out that definite difference exists between the reaction described above and that which takes place between vanadates and hydrazides. The latter occurs with both aliphatic and aromatic hydrazides and does not depend on the existence of any additional groups.

TABLE I

No.	Name of acid	colour-reaction
T-2	salicylhydroxamic	+++ violet
T-26	acetylosalicylhydroxamic	+++ violet
T-40	5-bromosalicylhydroxamic	+++ violet
T-95	3-methylsalicylhydroxamic	+++ violet
T-97	4-methylsalicylhydroxamic	+++ violet
T-100	5-methylsalicylhydroxamic	+++ violet
T-106	2-hydroxy-3-naphthohydroxamic	+++ violet
T-112	3,5-dimethylsalicylhydroxamic	+++ violet
T-139	8-hydroxy-7-quinolinhydroxamic	+ green-blue
T-143	3-methoxysalicylhydroxamic	+ brick-red
T-145	*p*-hydroxybenzhydroxamic	+ pink
T-151	1-hydroxy-2-naphthohydroxamic	+++ violet
T-162	*α*-naphthoxyacetohydroxamic	—
T-173	oleilhydroxamic	—
T-180	bromostearylohydroxamic	—
T-183	cholohydroxamic	—
T-184	dezoxycholohydroxamic	—
T-60	*p*-hydroxylaminobenzoic	—
T-107	phenyhydroxylaminopropionic	—
1	salicylic	—
2	salicylamide	—
3	benzhydroxamic	+ pink
4	propiohydroxamic	+ pink
5	valeriohydroxamic	+ pink
6	maliohydroxamic	+ pink

The structure of the coloured compound has yet to be investigated. So far, it has been found by S. Malinowski [10] that when 1 mol of vanadate is mixed with 2 mols of salicylhydroxamic acid, the reaction is quantitative. When concentration is high, a pigment can be precipitated. It forms a dark violet powder, soluble in hot water.

We use this reaction to determine the metabolism of salicylhydroxamic acid and its analogues in the living body.

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GEOLOGY

Upper Cretaceous Volcanism in the Carpathian Flysch Geosyncline

by

M. KSIĄŻKIEWICZ and T. WIESER

Presented by M. KSIĄŻKIEWICZ on February 22, 1954

By reason of the tuffs found interbedded in variegated marls [1], a Middle or Upper Cretaceous age was assigned to the volcanic rocks found, several years ago, in the Sub-Silesian nappe of the Western Carpathians. This hypothesis, which at first was based only on a few uncertain facts and was without palaeontological support, has recently been confirmed as a result of our work on the exotic rocks of Bachowice (Wadowice area). Here, in dark and variegated shales overlying green and red marls with Globotruncana and *Reusella szajnochae* Grzyb. (Campanian-Maestrichtian) occur numerous blocks already known to E. Tietze [2], among which volcanic rocks such as dacitic tuffs, spilites and basalts have been found. While examining these rocks one of us (T. W.) found, contained in thin slides, in dacitic tuffs small fragments of limestones with Globotruncana. Globotruncana limestones occur abundantly among the Bachowice exotics and are of Upper Cretaceous age, probably representing a full series of Turonian, Santonian and Campanian. In the tuffs the following species were determined (M. K.): *Globotruncana lapparenti* Brotzen, *G. arca* Cushman and *G. leupoldi* Bolli. The last two forms indicate that the limestone fragments in the tuffs are of Upper Senonian age. As the exotic blocks occur in the topmost part of the green Upper Senonian marls and in the Palaeocene dark shales, it may be concluded that the eruptions took place during the Campanian or shortly afterwards, anyway before the end of the Senonian and especially in the Palaeocene the tuffs were already eroded.

The volcanic rocks of Bachowice seem to form a series of eruptions beginning with basalts and spilites and followed by a more explosive stage during which dacitic tuffs were formed. These are the most common exotic rocks of Bachowice [3] and contain fragments of spilites. This sequence is in conformity with the course of volcanic cycles connected with orogenic movements in the geosynclinal stage which usually begins with basic lavas

and ends with eruptions of acid rocks. It is very probable that the eruptions were at least partially of a submarine character. This is indicated by the albitisation and carbonitisation of tuffs and spilites, the decomposition of lavas due to contraction caused by contact with cold water, and the association of volcanic rocks with carbonaceous rocks which is shown by transition to limestones through tuffaceous limestones, probably partly precipitated from sea water heated and agitated by eruptions. Graded and laminated bedding of the tuffs indicates an environment influenced by currents.

The occurence of volcanic rocks in the exotic series of Bachowice and their connection with the Sub-Silesian unit permit a tentative reconstruction of the geological structure with which the Upper Cretaceous volcanism is connected and of its regional position in the Carpathian geosyncline. The Upper Carboniferous beds have probably been directly deposited on the basement rocks of tonalites and diorites [3]. The Trias has not been found for certain at Bachowice, but the Jurassic is well developed and begins with the Bajocian and possibly with the Aalenian. The Oxfordian and the Kimmeridgian are bathyal with limestones containing abundant *Phylloceratidae*, *Lytoceratidae* and *Oppeliidae*. The Tithonian is not developed in the reef facies common among the exotic blocks of the Flysch zone but as pelagic limestones with *Calpionella* and ammonites. This type of sediment indicates that the Jurassic of Bachowice has been deposited in a vast and fairly deep trough [4]. Only in the Valanginian has it become more shallow.

The conglomerates and limestones with numerous species of Globotruncana constitute the next member of the Bachowice exotic series. As they contain blocks and pebbles of the Tithonian and Kimmeridgian limestones, they have apparently been deposited transgressively on the emerged Bachowice Jurassic. Therefore, on the deposition of the Upper Jurassic and of the probable Valanginian and possibly of other members of the Lower Cretaceous, so far not recognised in the Bachowice sequence, the area must have emerged and been subsequently submerged in the Upper Cretaceous, probably in the Turonian or Cenomanian. It is probable that the emersion was due to folding connected with the post-Middle Cretaceous folding of the Carpathian geosyncline. Owing to this folding, a geanticlinal ridge (cordillera) consisting of the Jurassic was created, but was soon inundated. The submersion was probably due to adjustment of the folded element to the new balance and this also might have been the cause of fracturing of the ridge. These fractures were utilized by ascending magma. Thus the Bachowice volcanism could have been an end product of the pre-Upper Cretaceous orogenic stage. It is, however, also possible that the eruptions were connected with rejuvenation of the movements of the ridge with the approach of the Laramide orogenic epoch. The Bachowice geanticline must have been affected by these movements, as it was uplifted again before the Palaeocene and eroded, and its reworked material deposited in the

Sub-Silesian Palaeocene beds. In both cases a geanticlinal ridge may be reconstructed, as has been done similarly for many areas and ages [5], forming an island arc with littoral or submarine volcanoes, situated far from the borders of the geosyncline.

It is probable that the Upper Cretaceous volcanism was more widely extended in the Flysch geosyncline than may at present be concluded from the traces found at Bachowice and in a few places belonging to the Sub-Silesian series; the volcanic rocks known from the Czarnohora Klippen, where, according to Z. Sujkowski [6], they are also associated with some Globotruncana limestones, may be regarded as being probably contemporaneous with the Bachowice eruptions. Tuffs reported by M. Filipescu [7] from the Senonian marls of the inner zone in the Roumanian Flysch Carpathians are approximately of the same age. In this way an axial zone may be visualized in the Flysch geosyncline with pelagic marls and limestones of the Upper Cretaceous [4], transformed into a geanticlinal ridge, which was a seat of volcanism at the and of the Cretaceous. In this picture the possible comagmatism of the teschenites with the Bachowice spilites remains a matter for conjecture.

At this moment it is not possible to say how long the volcanic activity, commenced in the Upper Cretaceous in the Carpathian Flysch, lasted. On this occasion it may be said that recently we found tuffs in the Krosno beds (Upper Eocene-Oligocene) but these rocks are connected with another, regionally different, volcanic cycle.

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